REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT DATE	3. DATES COVERED (From - To)
	June 25, 2001	Interim Report

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Sol-Gel Synthesis and Characterization of Molybdenum Oxide/Polypyrrole Hybrids	5b. GRANT NUMBER N00014-93-1-0245
	5c. PROGRAM ELEMENT NUMBER PR No: 01PR0086-00

6. AUTHOR(S)	5d. PROJECT NUMBER
Winny Dong and Bruce Dunn	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Bruce S. Dunn Department of Materials Science and Engineering University of California, Los Angeles Los Angeles, CA 90095	Technical Report #13

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
Office of Naval Research 800 North Quincy Street Arlington, VA 22217	11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT

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13. SUPPLEMENTARY NOTES
Published in: *Proceedings of the MRS Symposium on Organic/Inorganic Hybrid Materials*

14. ABSTRACT

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15. SUBJECT TERMS

molybdenum oxide, aerogel, inorganic/organic, electrochemical properties

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
U	U	U		6	19b. TELEPONE NUMBER (Include area code)

Standard Form 298 (Rev. 8-98)
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20010705 074

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Technical Report #13

Sol-Gel Synthesis and Characterization of Molybdenum Oxide/Polypyrrole Hybrids

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June 25, 2001

SOL-GEL SYNTHESIS AND CHARACTERIZATION OF MOLYBDENUM OXIDE/POLYPYRROLE HYBRIDS

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ABSTRACT

Monolithic Mo oxide/polypyrrole hybrid aerogels and xerogels were successfully synthesized through sol-gel methods. The PPy formed appears to be β-substituted. A 100 fold increase in electrical conductivity was observed for the hybrids (4×10^{-3} S/cm) as compared to the pristine MoO_3 gels (2×10^{-5} S/cm). An initial increase in Li^+ intercalation capacity is also observed for the hybrid. The electrical conductivity and Li^+ intercalation depend greatly on the concentration of Mo-trichloro alkoxide precursor and sol aging conditions. The hybrid aerogels have a density of 0.5 g/cc and a surface area of 120 m^2/g. The as-formed gels are amorphous and crystallize to the orthorhombic MoO_3 phase at 375°C.

INTRODUCTION

Polypyrrole (PPy) and molybdenum compounds have attracted the attention of electrochemists for different reasons. Polypyrrole has been proposed as a potential candidate for the active cathode material in polymer batteries. This is because PPy can be oxidized to have electrical conductivity between 40-100 S/cm [1], and its films can be easily produced on various substrates by electropolymerization [2]. Molybdenum compounds, such as MoO_3 and MoS_2, are of interest for Li batteries due to their good intercalation properties. The main drawback for both Mo compounds is the low electrical conductivity [3,4].

In prior work, PPy and amorphous MoS_3 were grown together through electrodeposition to form a composite material [4-7]. The goal was to electrochemically form a compound with good intercalation and electrical conductivity properties. The same method could not be used for the combination of PPy with MoO_3, however. This is because the redox potential of MoO_3 (3.2 V) is not sufficient to oxidatively polymerize pyrrole during the insertion reaction [8]. The formation of nanocomposites with MoO_3 and various conducting polymers (such as poly(aniline), polypyrrole, and poly(para-phenylene)) has been reported by Nazar et al through an ion exchange method where the monomer is inserted between the MoO_3 layers and oxidatively polymerized [8,9].

This paper presents novel synthesis techniques through which MoO_3/PPy hybrid aerogels and xerogels have been synthesized successfully. The sol-gel technique provides a method where molecular mixing of the different components can occur while yielding a high surface area end-product. Through this technique, it is anticipated that the molecular level mixing can better maximize the advantages of both compounds while enhancing intercalation reactions through the high surface area materials. Preliminary data show that the hybrid does indeed have higher electrical conductivity and higher initial lithium capacity as compared to that of MoO_3 gels. Physical, electrical, and electrochemical properties of the MoO_3/PPy hybrids are reported.

EXPERIMENTAL METHODS

There were two general routes taken to synthesize the MoO_3/PPy hybrid. Both involve first forming a molybdenum oxide sol, details of which were reported previously [10]. In the first route (samples A), the pyrrole monomer (Aldrich) was added immediately upon formation of the sol and then allowed to age in closed containers. Gelation occurred in approximately 1 week. In the second route (samples B), the sol was allowed to age in closed containers first, then shortly before gelation the pyrrole monomer was added. Gelation occurred within 1-3 days after the addition of the monomer. Concentration of the monomer ranged from 0.3 to 0.6 moles of Py/Mo for both types of samples.

After gelation, the samples were aged in closed containers for 1-2 weeks. Aerogels were formed by supercritically drying as described by Chaput et al. [11]. Xerogels were formed by opening the containers to air for 2-3 days then heat treating at 100°C for 2-3 hours.

Chemical analysis was performed by Galbraith Laboratories, Inc. Nitrogen gas adsorption analysis (Micromeritics, ASAP 2010) was used to determine the surface area of the aerogels and xerogels by the BET method. The BJH method was used in determining the average pore diameter. The bulk densities of the gels were determined with a Hg pycnometer while the skeletal densities were measured with a gas pycnometer (Micromeritics, AccuPyc 1330). Transmission electron microscopy (JEOL, 100CX) was used to help determine the structure and morphology of the gels. FTIR measurements (Nicolet, 510P) were used to establish bond formation of the hybrid.

The electrical conductivity of the MoO_3/PPy hybrid gels was measured from 150°C to 30°C by the complex impedance method (Hewlett Packard 4284A LCR meter). For these measurements, powders of the hybrids were pressed into pellets and gold electrodes sputtered on opposite sides. The electrochemical behavior was determined for a crushed gel mixed with conductive carbon powder and a PVDF binder (80: 20: 5 weight ratio, respectively). The sweep rate was 0.1 mV/sec with 1M $LiClO_4$ in propylene carbonate as the electrolyte.

RESULTS

TGA data and chemical analysis confirm the presence of the polymer in both hybrids A and B. TGA data shows an initial 10% weight loss around 100°C which is attributed to the loss of organics from the solvent. A more gradual loss which occurs between 125 and 325°C is most likely due to the remaining organics and physically adsorbed water. Polypyrrole starts to decompose at 325°C [12], corresponding to the observed 15% wt. loss between 325 and 400°C. The composition of the as-prepared gel based on the TGA data and chemical analysis roughly corresponds to 1.0 MoO_3:0.4 PPy:0.4 H_2O:0.3 CH_3NH_2 with a slight excess of carbon and hydrogen. Cl⁻ ions are believed to be incorporated into the PPy structure. Chemical analysis shows that Mo oxide/PPy hybrids retain most of the chlorine present from the $MoCl_3(OPr^i)_2$ precursor (approximately 1 Cl⁻/Mo). This is in contrast to the MoO_3 gels prepared with the same concentration of the $MoCl_3(OPr^i)_2$ precursor, which only contain 0.3 Cl⁻/Mo. Density and surface area data are listed in Table I.

TEM and XRD data show that the initial gel is amorphous and that it crystallizes to the orthorhombic phase at 375°C. At this temperature all the polymer has been decomposed, leaving MoO_3. In the amorphous XRD, the two broad peaks at $2\theta = 25$ and 30° can be attributed to the polypyrrole rings [12, 13].

FTIR data (Figure 1) indicate that the polypyrrole formed in both types of samples is most likely β-substituted, where a methyl group replaces the H on one or both β carbons. This is because the typical A' (1550 cm⁻¹) and B' (1460 cm⁻¹) FTIR peaks for unsubstituted PPy [14,15] are not observed. However, the peak for C-H symmetric deformation (1400 cm⁻¹) is much stronger in the hybrid system than in the Mo oxide system verifying the presence of polypyrrole in the system. The spectra for the two hybrids are fairly similar except for the absorptions in the 790-720 cm⁻¹ and 970 cm⁻¹ regions that are present in B and not in the A samples. The presence of these peaks have been assigned to a more highly oxidized PPy [15]. Therefore, the PPy in B samples are most likely more highly oxidized than that in A samples.

Table I. Density and surface area data for MoO_3 and MoO_3/PPy hybrid gels

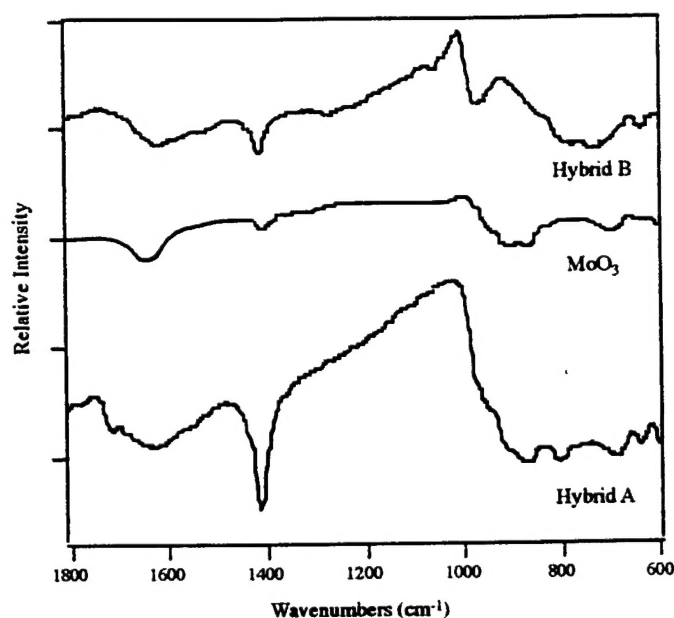| Sample	Density (bulk) (g/cc) ± 0.05	Density (Matrix) (g/cc) ± 0.1	Surface Area (m²/g) ± 10	Avg. Pore Diameter (Å)± 10
MoO_3 xerogel	1.5	3.0	< 10	80
MoO_3 aerogel	0.2	3.7	180	500
Hybrid B xerogel	1.3	2.2	< 10	
Hybrid B aerogel	0.5	3.3	120	

Figure 1. FTIR spectra for MoO_3 and MoO_3/PPy hybrid gels.

Electrical conductivity (Figure 2 and Table II) and activation energy (Table II) of hybrid A was similar to that of MoO_3 gels. However, hybrid B showed a marked improvement. Its electrical conductivity (4×10^{-3} S/cm at room temperature) was approximately 100 times higher than the MoO_3 gels and about 10 times higher than values reported for the hybrid PANI-MoO_3 (5×10^{-4} S/cm) [8]. Its activation energy was also lower, similar to that of pure polypyrrole polymerized in ethanol. Complex impedance spectra indicated purely electronic conduction for this material, as the data give a single point on the real axis. The electrochemical behavior (Figure 3) was influenced by the enhanced electrical conductivity. Hybrid A behaved similarly to amorphous MoO_3 gels in that it exhibited the same broad peak on intercalation (2.0 V) and de-intercalation (2.2 V). In contrast, hybrid B exhibited significantly different intercalation behavior, having both broad and sharp intercalation peaks (at 2.5 and 2.0 V, respectively). Hybrid B intercalated 1.68 Li/Mo upon the first cycle. However, only 58% of that capacity was reversible.
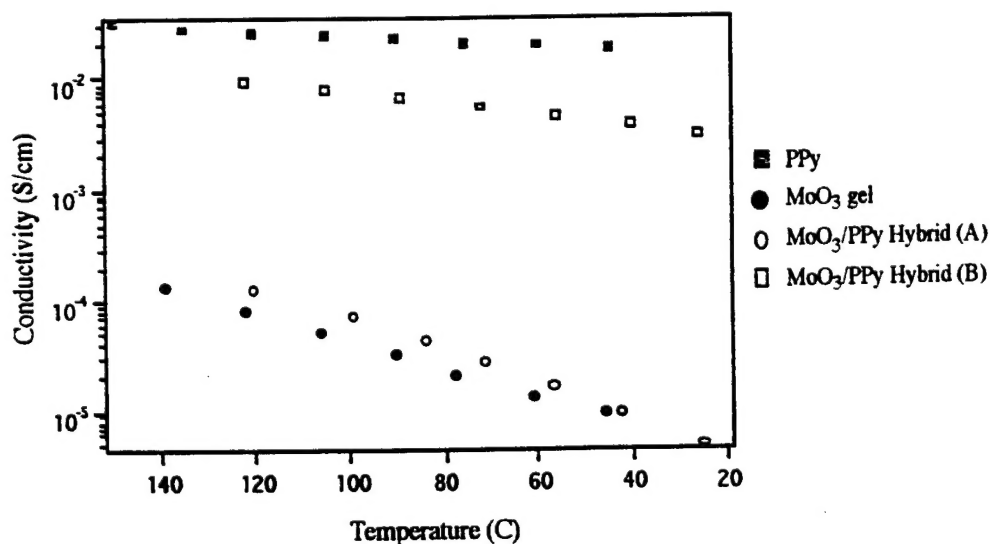

Figure 2. Electrical conductivity of MoO_3/PPy hybrids compared to that of pure MoO_3 gel and polypyrrole.

Table II. Electrical and electrochemical properties of MoO$_3$/PPy hybrids compared to that of pure MoO$_3$ gel.

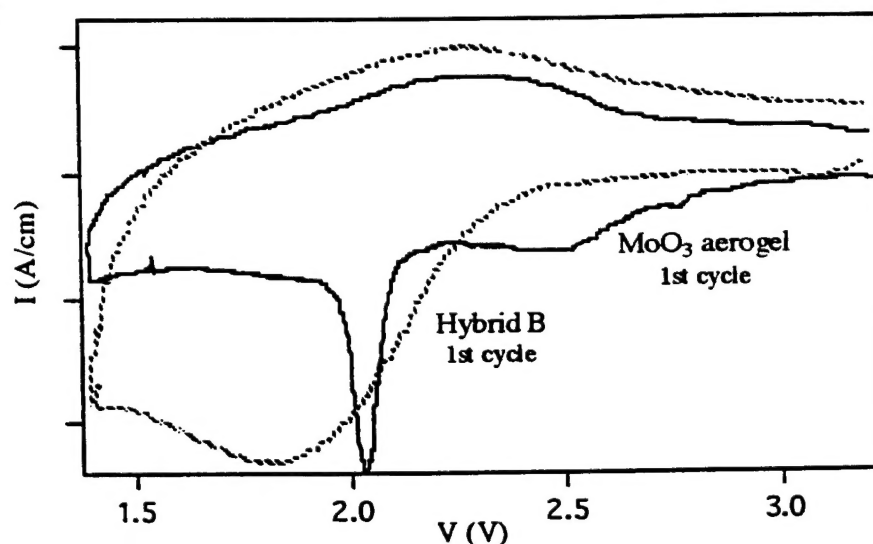| Sample	Electrical Conductivity (S/cm)		Act. Energy (eV)	Lithium Capacity (per Mo)	
	at 150°C	at 40°C		1st cycle	2nd cycle
MoO$_3$*	3×10^{-4}	2×10^{-5}	0.34	1.5	1.2
MoO$_3$**	4×10^{-4}	8×10^{-5}	0.33	1.1	0.8
Hybrid A	4×10^{-4}	8×10^{-6}	0.32	1.1	0.7
Hybrid B	1×10^{-2}	4×10^{-3}	0.10	1.7	1.0

* nano-crystalline
** amorphous

Figure 3. Cyclic voltammetry of MoO$_3$/PPy hybrid as compared to that of MoO$_3$ aerogel.

DISCUSSION AND CONCLUSIONS

There are two important factors that determine the electrical conductivity of the final hybrid sample. First, there is the concentration of MoCl$_3$(OPr^i)$_2$. Low concentrations of the trichloro-alkoxide result in low conductivity due to insufficient dopant. An excess of the trichloro-alkoxide results in long gelation time and poorly gelled samples. The ideal composition has been found to be 1 Mo(OPr^i)$_5$: 1 MoCl$_3$(OPr^i)$_2$. The Cl$^-$ ions are found to be necessary as counteranions. Upon first oxidation of the pyrrole, polymerization occurs. Upon further oxidation, bipolarons are introduced into the system and the polymer becomes conductive [16]. To stabilize the polymer in this step, a counteranion such as Cl$^-$ needs to be incorporated into the structure. The doping of polypyrrole by Cl$^-$ has been reported [4].

The second factor is the sol aging conditions. Gels that were not aged prior to the addition of the pyrrole monomer (A samples) behaved similarly to pure Mo oxide samples both electrochemically and electrically. Gels that were aged (B samples) exhibited both increased electrical conductivity and initial lithium capacity. The reducing properties of the pyrrole monomer increases the gelation rate of the molybdenum oxide matrix. This changes the structure of the matrix and is the main difference between hybrids A and B. In the case of sample B, the molybdenum oxide network has had a chance to partially form before the addition of the pyrrole, allowing both the polypyrrole and the molybdenum oxide to form a semi-continuous network through the gel. It is clear in the TEM micrograph (Figure 4a) that all the particles are in contact with each other, allowing a continuous path for the electrons. But in the case of sample A (Figure 4b), addition of the monomer immediately after the formation of the sol caused the molybdenum oxide matrix and the polypyrrole to form distinctly separate phases. This, in effect, prevents the

formation of a continuous path for electrons. Therefore the polypyrrole did not contribute to the electrical conductivity.

The electrochemical results show only a slight benefit from the hybrid approach. The semi-continuous polypyrrole network in hybrid B contributed to lithium intercalation through the broadened and shifted intercalation peak in Figure 3. Although the lithium capacity was enhanced for the first cycle, it was not reversible and subsequent cycles fell below that of MoO_3. This behavior may be due to the PPy being irreversibly reduced upon intercalation with Li^+ ions causing the expulsion of the Cl^- counteranions [4].

Another observation was that the PPy formed through this method is most likely a β-substituted PPy. This explains the low electrical conductivity of hybrid B compared to that of pristine PPy (40-100 S/cm) grown electrochemically in acetonitrile [16]. The lowered conductivity in the substituted PPy can be due to the loss of planarity or increased chain separation [17]. The position of the substitution also plays a role. Methyl groups attached to the nitrogen sites can cause the polymer to be extremely non-planar. Whereas substituting at the C positions with small groups (CH_3) does not cause too much loss in planarity [16].
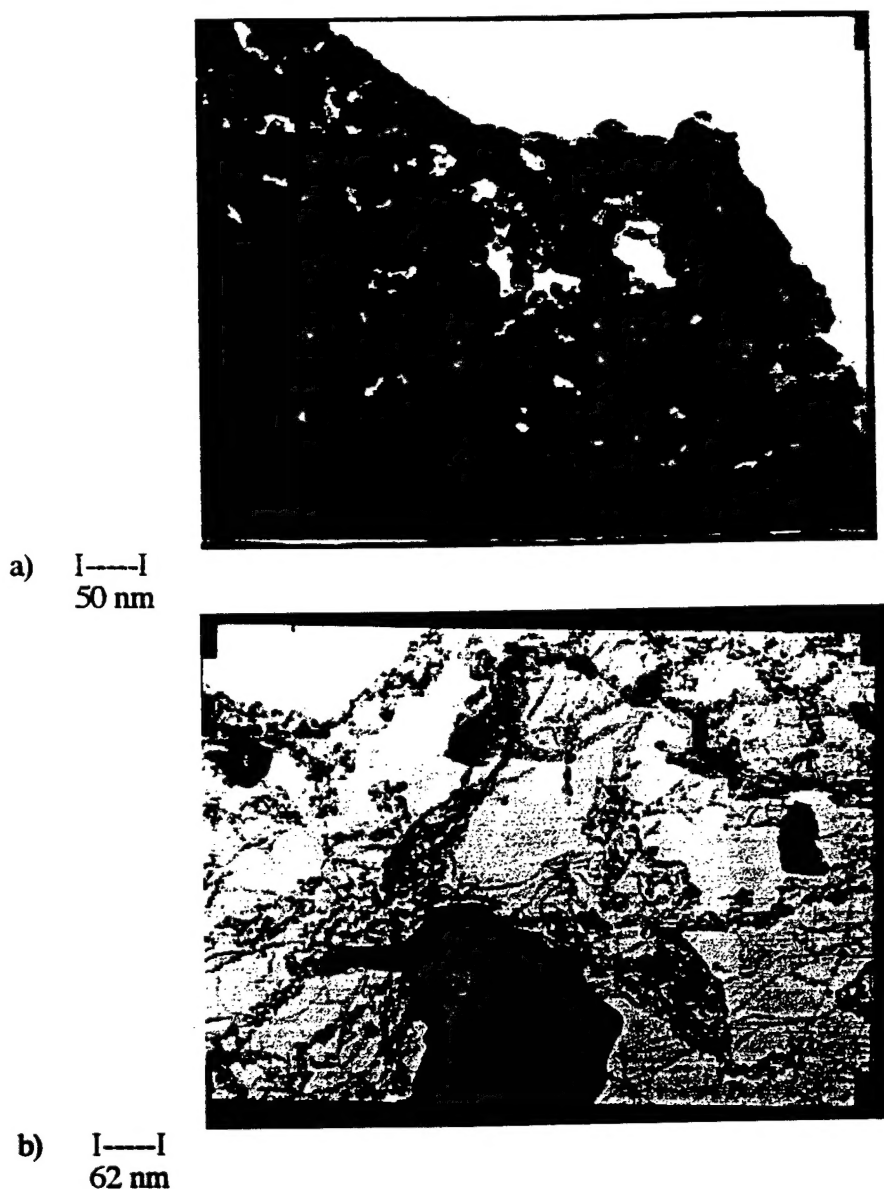

a) I----I
50 nm

b) I----I
62 nm

Figure 4. TEM micrographs of a) sample B and b) sample A

ACKNOWLEDGEMENTS

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